AIP Applied Physics Letters

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Citation: Applied Physics Letters **73**, 617 (1998); doi: 10.1063/1.121874
View online: http://dx.doi.org/10.1063/1.121874
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/73/5?ver=pdfcov
Published by the AIP Publishing

Hard hydrogenated carbon films with low stress

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(Received 14 November 1997; accepted for publication 29 May 1998)

Analysis of hard *a*-C:H films with low stress prepared by methane plasma decomposition is reported. Films with hardness as high as 14 GPa and stress as low as 0.5 GPa were obtained. These films have a high Raman I_d/I_g ratio (~1.0), and small Tauc's band gap (~0.4 eV). This letter also supplies strong evidence that the subimplantation deposition model, used to explain the formation of *ta*-C and *ta*-C:H films, is also valid for *a*-C:H films deposited by methane plasma decomposition. It is proposed that the rigidity of the films is basically provided by a matrix of dispersed cross-linked sp^2 sites, in addition to the contribution of the sp^3 sites. © *1998 American Institute of Physics.* [S0003-6951(98)02431-0]

Hard hydrogenated carbon films have numerous potential applications like wear resistant coatings, magnetic recording disk, antireflective films, photoluminescent diode, etc. One of the main problems that hinders these applications is the high internal stress, usually present in films with high hardness. It is well known that high stress is responsible for the poor adhesion of hard amorphous carbon films. Therefore, the production of films with low stress is extremely important for technological application. Recently, there have been some studies aimed at the reduction of the stress, in films with high hardness. Some success has been achieved by incorporating impurities, like nitrogen and boron, into the carbon network.[1,2] In this letter, we report the production of hard hydrogenated carbon films, with a remarkable stress reduction without a significant change of the film hardness. In addition, the films were also deposited at relatively high deposition rates and without the incorporation of any additional element into the film network. Furthermore, this letter provides a major support for the subimplantation model to explain *a*-C:H films formation using plasma decomposition.

The films were produced in a conventional 13.56 MHz rf sputtering system by methane gas decomposition. They were deposited on the cathode electrode. All films were prepared at room temperature, and constant CH_4 gas pressure of 1.0 Pa. The bias voltage was varied in the −100 V to −1200 V range. The thickness of the films measured by a Dektak profilometer was about 1 μm. The hardness was obtained from a nanoindenter using a set of different loads in the 0.5–90 mN range. Raman spectroscopy were obtained with a Jobin Ybon T64000 spectrometer in the backscattering configuration, at room temperature. Elastic recoil detection analysis (ERDA) was performed to determine the hydrogen concentration. The optical Tauc's gap was determined from the transmission spectra, in the 300–2500 nm range, using a Perkin-Elmer λ9 spectrometer. Stress measurements were taken from films deposited on $4\times25\times0.4$ mm^3 *c*-Si bars, using the well known Stoney's equation.[3]

The deposition rate, Fig. 1(a), increases more than one order of magnitude, from 0.02 to 0.23 nm/s, as the negative bias voltage increases from −100 V to −1200 V. On the other hand, the Tauc's gap decreases about 0.7 eV in the same range, Fig. 1(b). The decrease of the Tauc's gap is consistent with the increase of the relative Raman intensity ratio of the *D* over *G* band (I_d/I_g), and the reduction of the hydrogen concentration [Fig. 1(c)]. The intrinsic stress (Fig. 2) reaches a maximum in the −100 V to −200 V bias range. Above −200 V the stress decreases monotonically. The highest stress obtained was 2.5 GPa at −120 V bias, a value typical for hard carbon films. Those films start to delaminate

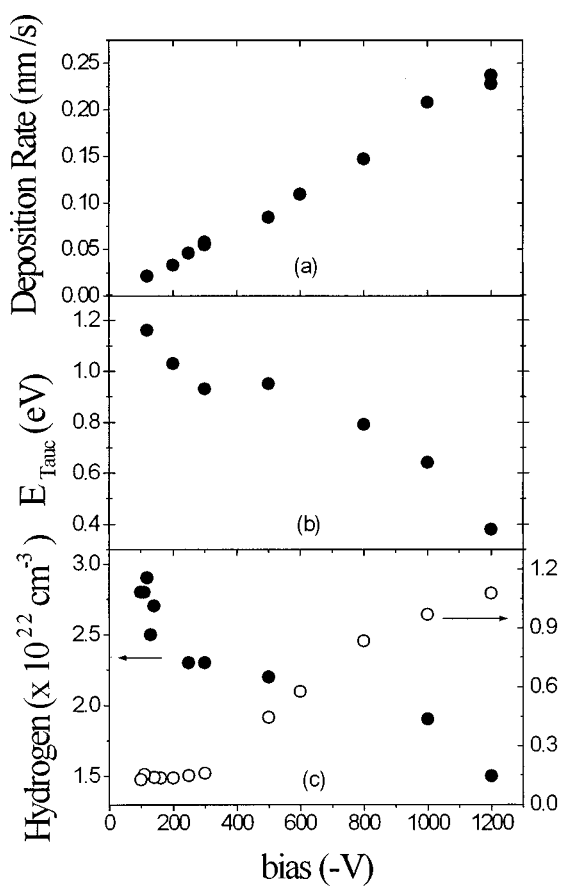

FIG. 1. Deposition rate (a), Tauc's gap (b), hydrogen concentration and Raman I_d/I_g ratio (c) of *a*-C:H films as a function of the negative bias voltage.

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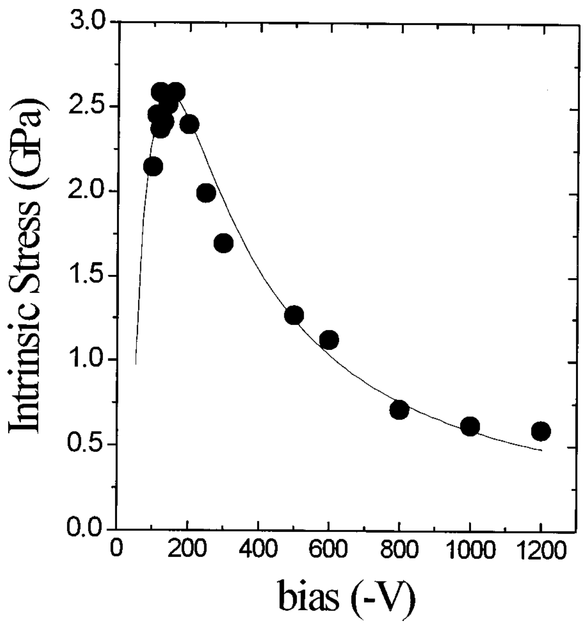

FIG. 2. Intrinsic stress vs negative bias voltage of the a-C:H films. The solid curve represents the fitting of Eq. (1) using the Davis model (Ref. 10).

from the substrate a few hours after being deposited. On the other hand, for high bias voltage the stress is quite low, about 0.5 GPa, resulting in very stable films. Although the deposition rate and stress varies remarkably in the bias range investigated, the hardness decrease is much smaller than that reported by Jiang *et al.*[4] for hard a-C:H carbon films prepared using a polarized rf glow discharge system for the same bias range, see Fig. 3.

The most important result obtained in this work was the deposition of a-C:H films with good mechanical properties. For example, at a bias of -1200 V, a film with reasonable high hardness of 14 GPa, with very low stress of 0.5 GPa,

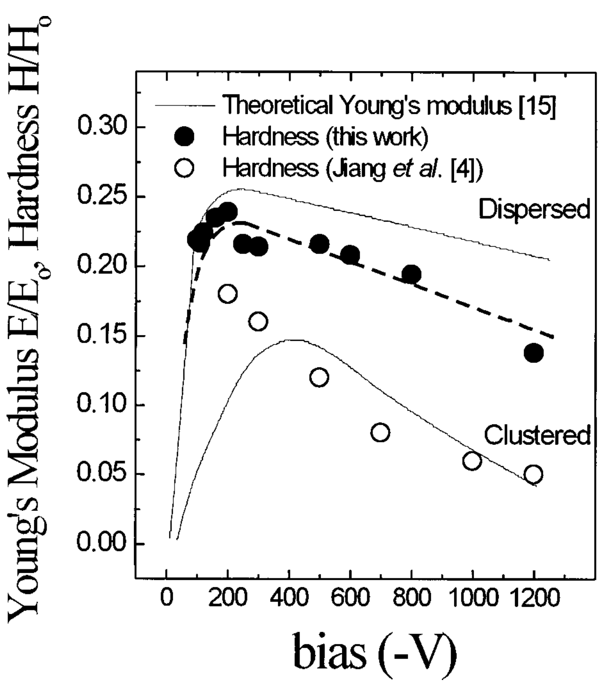

FIG. 3. Normalized theoretical Young's modulus and hardness vs negative bias voltage of a-C:H films. E_0 and H_0 are the Young's modulus and hardness of diamond, respectively.

prepared at a high deposition rate of 0.23 nm/s, was obtained. At this preparation condition, hard and almost stress free films as thick as 5 μm could be prepared. This film did not delaminate from the substrate. As far as the authors are concerned, there are no equivalent films reported in literature with similar properties. Recently, Chhowalla *et al.*[2] obtained a high stress reduction, from 10 to 2 GPa, by incorporating 2%–4% of boron into the film network. Although this is a considerable reduction of stress, 2 GPa is still high. Films with this stress intensity delaminate from the substrate with time, which is not the case for our films prepared at high bias. These films are still well adhered to the substrate several months after deposition. In addition, the stress reduction of our films was achieved without incorporating impurities of other elements into the film.

The subimplantation model has been used to understand the deposition mechanism of high tetrahedral carbon films, ta-C and ta-C:H.[5–10] Robertson proposed an equation relating the film density to the ion bombarding energy.[9] A similar equation has also been proposed by Davis to explain the dependency of the compressive stress on the ion energy.[10] Both models support the subimplantation model. The stress as a function of the ion energy was found as:[10]

$$\sigma \propto \frac{c\sqrt{E}}{R/j+0.016p(E/E_0)^{5/3}}, \tag{1}$$

where c is a constant, E is the ion energy, E_0 is the activation energy of the relaxation process, j is the ion flux, R is the depositing flux, and p is a material-dependent parameter which is of the order of 1 according to the thermal spike model.

The sputtering bias voltage does not represent the effective energy of the ions striking the film surface, as required in Eq. (1). However, considering that at 1 Pa the ion collisions in the sheath width are not significant,[11] a good approximation of the ion energy is $E \approx V_{\text{plasma}} - V_{\text{bias}}$,[12,13] where V_{plasma} is the plasma potential and V_{bias} is the sputtering bias voltage. The stress data of Fig. 2 were then fitted using Eq. (1), which clearly matches the data. The best fitted parameters found were $c=0.58$, $R/j=1.59$, $p(E_0)^{-5/3}=0.019$ and $V_{\text{plasma}}=44$ V. The product $p(E_0)^{-5/3}=0.019$ is very similar to that, $p(E_0)^{-5/3}=0.012$, found in the works of Fallon *et al.*[7] from ta-C films, and Weiler *et al.*[8] from ta-C:H. Fallon *et al.* suggest that E_0 has a value between 2.5 and 3 eV due to the film thermal stability, which gives $p \approx 0.1$ for both their data and ours. The plasma potential found in the fitting procedure is reasonable and similar to the typical values reported in the literature,[12,13] giving support to the correction used. The R/j flux ratio is also of the same order experimentally found by Kleber *et al.* using methane gas decomposition.[14] The highest stress and hardness obtained were at a bias voltage of about -120 V, corresponding to an ion energy of about 160 eV. This ion energy is similar to those found in the ta-C (140 eV) and ta-C:H (92 eV).[7,8] In short, the parameters found in the fitting procedure, altogether with the similarity of the maximum energy position and the sharp peak obtained, support the interpretation that the deposition of a-C:H films using methane gas decomposition on the cathode of a rf sputtering system is, indeed, controlled by ion subimplantation process, as in the case of *ta*-C and *ta*-C:H films.

The solid curves displayed in Fig. 3, represent the theoretical Young's modulus calculated by Robertson[15] for hydrogenated amorphous carbon, using the coordination data reported by Tamor *et al.*[16] The "dispersed" curve represents films where sp^2 and sp^3 sites are distributed at random without a preferential structure formation, while the "clustered" one includes large sp^2 clusters. Different from the behavior of the hardness data (which is related to the elastic modulus) of Jiang *et al.*, the behavior of our data is better represented by the theoretical Young's modulus expected for the dispersed structure. These results do not exactly agree with the cluster model proposed by Robertson,[15] but are in agreement with recent experimental and theoretical findings which contradict the formation of large clusters. Neutron diffraction and molecular dynamics simulation suggest that the most probable structure formation of sp^2 sites would be in the olefinic rather than aromatic groups.[17,18] Recently, Robertson proposed a modification of the cluster model limiting the clusters size to single sixfold sp^2 rings and chains of sp^2 sites rather than large islands of fused sixfold rings, as initially suggested.[19]

The reduction of the Tauc's gap, from 1.2 to 0.5 eV [Fig. 1(b)], as the bias voltage varies from -100 V to -1200 V, can be explained as due to increasing number of sp^2 sites.[19] This is also supported by a significant increase, from 0.2 to 1.2, of the relative Raman intensity ratio of the D over G band (I_d/I_g) in the same bias voltage range [see Fig. 1(c)]. A high I_d/I_g ratio has been associated with high concentration of sp^2 sites, though the origin of both D and G band are not well understood.[20–22] Considering the reduction of the Tauc's gap and hydrogen concentration and the increase of the I_D/I_G ratio (Fig. 1), the concentration of sp^3-hybridized-carbon bonded to carbon (sp^3 C–C) is expected to decrease as the bias increases.[19–22] Thus, the reduction of stress, as the bias increases, is probably related to a significant decrease in the concentration of sp^3 C–C sites.[23] Surprisingly, hard films were obtained even at high bias. The rigidity of these films is probably provided by a cross-linked structure of the sp^2 sites, as in *a*-C prepared by sputtering, which has only about 5% of sp^3 sites, and hardness of 15 GPa.[24] The role of the sp^3 C–C sites would be to strain the cross-linked structure (generating the compressive stress), and also to give some contribution to the material hardness.[25] Recently, Amaratunga *et al.* also reported the preparation of carbon films whose hardness is maintained by the interlinking of carbon nanoparticles.[26]

In conclusion, we produced hard amorphous hydrogenated carbon film with low stress at a high deposition rate. These properties can be of significant interest for technological applications. We also found strong evidence that the subimplantation process controls also the film formation in the plasma gas decomposition process. We suggest that the film structure is composed of a matrix of dispersed cross-linked sp^2 sites, which provide the network rigidity. Although the sp^3 C–C sites also contribute to the material hardness, their main role is to provide compressive stress for the films.

This work has been supported by the following Brazilian Agencies: CNPq, FAPESP, and PADCT. The authors are in debt to Professor C. M. Lepienzsky for the nanoindentation hardness measurements and also to Professor F. L. Freire for the ERDA measurements.

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